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EPA (Environmental Protection Agency) Recommended Practice for Naming I/M (Inspection/Maintenance) Calibration Gas

(U.S.) Environmental Protection Agency
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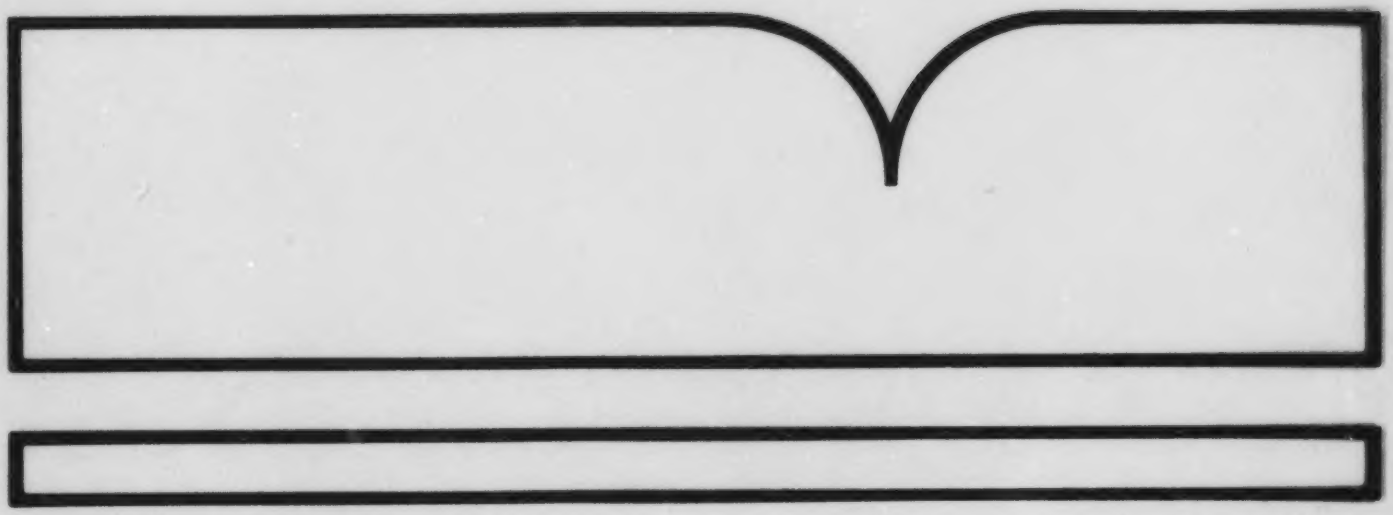

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Technical Report

EPA RECOMMENDED PRACTICE FOR NAMING I/M CALIBRATION GAS

September 1983

Technical Support Staff
Emission Control Technology Division
Office of Mobile Sources
Office of Air and Radiation
U. S. Environmental Protection Agency
Ann Arbor, Michigan 48105

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Appendix 1 Section 85.2217 of Emission Control System Performance Warranty Regulations

Appendix 2 Overview of Analytical Procedures

Appendix 3 Alternative Procedures for Compensating for Instrument Drift

Appendix 4 Accuracy Discussion

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16. ABSTRACT

This volume the second of a two volume report presents a set of procedures scientific gas manufacturers can use to blend, analyze, and label calibration gases for infrared inspection analyzers used in motor vehicle inspection and maintenance (I/M) programs.

The procedures are intended to be used on gases a manufacturer labels with the phrase "made in accordance with the EPA Recommended Practice For Naming I/M Calibration Gas." EPA has established no legal requirements that gas manufacturers follow this set of procedures. However, claims by a gas manufacturer that a gas has been made in accordance with this set of procedures may create rights and obligations under existing State or Federal law, particularly those related to fair marketing procedures and product warranties.

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1.0 INTRODUCTION

This report presents a set of procedures scientific gas manufacturers can use to blend, analyze, and label calibration gases for infrared inspection analyzers used in vehicle inspection and maintenance (I/M) programs. The procedures are intended to be used on gases a manufacturer labels with the phrase "made in accordance with the EPA Recommended Practice For Naming I/M Calibration Gas." EPA has established no legal requirement that gas manufacturers follow this set of procedures. However, claims by a gas manufacturer that a gas has been made in accordance with this set of procedures may create rights and obligations under existing State or Federal law, particularly those related to fair marketing practices and product warranties.

EPA encourages States and other I/M authorities to procure gases named according to this practice for their own use, and to require inspection stations to procure them to ensure they are obtaining accurate calibration gases which meet the terms of the Emission Control System Performance Warranty, and to improve the general quality of their I/M programs. EPA recognizes that there may be many other techniques and analytical procedures for blending and naming I/M gases which could achieve the same results as this recommended practice. However, these are the only techniques that may be followed if a gas manufacturer is to label a gas with the phrase "made in accordance with the EPA Recommended Practice for Naming I/M Calibration Gas".

Propane, hexane, carbon monoxide (CO), and carbon dioxide (CO_2) can be named with these procedures as two component mixtures of one of the components in nitrogen (N_2), or as multi-component mixtures such as CO and propane in N_2 or CO, hexane, and CO_2 in N_2. The possible combinations are shown in Table 1.

Table 1

Possible Mixtures of I/M Gases
Covered by the Recommended Practice

Number of Components		
Two	Three	Four
Propane in N_2	Propane, CO in N_2	Propane, CO, CO_2 in N_2
Hexane in N_2	Hexane, CO in N_2	Hexane, CO, CO_2 in N_2
CO in N_2	Propane, CO_2 in N_2	
CO_2 in N_2	Hexane, CO_2 in N_2	
	CO, CO_2 in N_2	

A separate report entitled "EPA Recommended Practice for Naming I/M Calibration Gas: A Discussion For I/M Programs" (EPA-AA-TSS-83-8-A) discusses issues concerning calibration gas which are of interest to States and other I/M authorities. The body of this report discusses the actual procedures gas manufacturers must use. The Appendix contains the relevant part of the Emission Performance Warranty Regulations which require traceability of ±2.0% to NBS for gases used to calibrate I/M analyzers, an overview of the analytical procedures, an explanation of an alternative procedure for accounting for instrument drift, and a discussion of techniques used to estimate the accuracy of gases named according to this practice.

2.0 BACKGROUND

An inspection and maintenance (I/M) program is a State or locally run program in which registered vehicles are required to obtain and pass a tailpipe emission inspection on a periodic basis. Vehicles that have tailpipe emissions greater than State or locally established emission standards are required to obtain maintenance to pass that standard. The emission test (called a "short test") can be conducted by the State (or locality) or a contractor to the State, and this is referred to as a "centralized program." The emission test can also be conducted by private garages which are licensed by the State. This latter system is called a "decentralized" program.

The primary inspection and diagnostic tool of these I/M programs is a non-dispersive infrared (NDIR) analyzer which is capable of determining the concentrations of hydrocarbons (as hexane), carbon monoxide, and, in some cases, carbon dioxide in raw vehicle exhaust. These analyzers need periodic calibration and maintenance to keep their accuracy, as age, operator misuse, or changes in pressure, temperature, and other operating variables can render them inaccurate.

Many analyzer manufacturers recommend a periodic check of their analyzers with a calibration gas. State or local I/M program regulations also require a periodic calibration check. This check is performed by flowing a calibration gas of known concentration into the analyzer and determining whether the analyzer is reading this calibration gas correctly. If it is not reading this gas correctly, then a simple adjustment (i.e., a calibration) of the analyzer can usually be performed which will result in the analyzer being accurate again. However, the accuracy of the calibration gas used is very important in determining analyzer accuracy with this maintenance check. If the labeled concentration of the calibration gas is significantly different from the true concentration in the cylinder, the analyzer could become significantly misadjusted. An operator who had performed the calibration would be unaware that he/she had actually misadjusted the analyzer, since he/she trusted the label on the calibration cylinder to be correct.

2.1 EPA Regulations Concerning Calibration Gas Accuracy

EPA has promulgated Emission System Performance Warranty Regulations for 1981 and later vehicles which entitle a vehicle owner to emission-related repairs at the manufacturer's expense if, among other things, the vehicle fails an "approved" emission short test. One condition is that the analyzer used to conduct the emission short test must be checked with gases "traceable to NBS standards $\pm$2.0%"

within a week of the test (40 CFR 85.2217). The relevant portion of this page is provided in Appendix 1 to this document. There are other requirements for these gases in the Warranty regulations; however, these are of interest more to States ordering gases than to manufacturers producing gases and are discussed in the companion report, EPA-AA-TSS-83-8-A. EPA thinks that many States implementing I/M programs will want to make Warranty protection available to consumers participating in their I/M programs. Consequently, these States will try to make sure that the gases used to periodically calibrate analyzers used in the I/M programs meet the Warranty requirement of having an accuracy of ±2.0% to NBS standards.

2.2 EPA Efforts to Help States Meet Warranty Requirement for Gas Accuracy

In order to improve the general quality of I/M programs, and to help States in meeting the accuracy requirement of the Warranty with respect to calibration gas used to check emission analyzers, the EPA has published this Recommended Practice which States can require gas manufacturers to follow in naming and labeling calibration gas for the I/M programs in those States. A State requirement would be imposed directly by the State in its own purchases of gas and/or indirectly by establishing rules and regulations which require other I/M gas users (contractors or licensed inspection stations) to buy only gas that the manufacturer certifies was named and labeled according to this Recommended Practice.

3.0 DISCUSSION OF RECOMMENDED PRACTICE

3.1 Analysis of Pure Components

Scientific gas manufacturers must follow certain procedures in ordering and analyzing pure components used to make I/M calibration gas. First, the impurity concentrations in the nitrogen used as a diluent or a gas to establish instrument zero shall not exceed 1 ppm equivalent carbon response, 1 ppm CO, 0.04% CO_2, and 0.1 ppm nitric oxide. These conform to the existing Federal regulation specifications for zero gases (40 CFR 86.114-78). Propane or hexane used must be "instrument grade" which is certified to be 99.5% propane or hexane, and the balance will be primarily other hydrocarbons (e.g., methane, iso-butane, butane and ethane). An analysis must be performed of this bulk propane or hexane to determine, in fact, that the gas used is at least 99.5% pure. Lastly, the carbon monoxide and carbon dioxide used must have a total hydrocarbon (THC) count which must not exceed 100 ppm.

Although these specifications for the pure components might seem moderately stringent when one considers that the dilution of the propane, carbon monoxide and carbon dioxide with nitrogen will result in these trace components (particularly methane) having very little effect on the resultant accuracy of the I/M span gas, they nonetheless contribute to error in naming the I/M calibration gas and should be limited. Also, the small extra cost of the components ordered and analyzed to these specifications will have virtually no effect on the overall cost of making the I/M calibration gas. The bulk of the cost in making an I/M calibration gas is incurred in filling and analyzing the final blend.

3.2 Cylinders and Waiting Time

Any size low pressure or high pressure cylinder may be used as a container for I/M calibration gas named according to this Recommended Practice; however, the cylinders must be constructed of either steel or aluminum. Aluminum must be used for mixtures containing CO with concentrations less than 1.0% CO unless the gas manufacturer can provide statistically valid data to show that the stability of the gas mixture is not degraded by using other types of cylinders. High pressure cylinders must be fitted with CGA-350 valves. Low pressure cylinders must be fitted with a CGA 1/4-inch flare-fitting valve. The use of these valves will allow I/M calibration gas users to switch suppliers (gas manufacturers) without having to purchase new regulators.

In some cases, an incubation period is necessary to order to ensure the accuracy of the mixture. For CO-CO_2-propane mixtures in dry nitrogen, the only potential problem is nonhomogeneous mixtures. In the case of high pressure cylinders, once the cylinders are filled, they must be rolled and/or convection heated for a period of 1 hour to ensure homogeneity. In the case of low pressure containers, the gas mixtures must originate from one homogeneous, well characterized bulk mixture; therefore, no incubation period is needed.

3.3 Instrument Preparation and Calibration

3.3.1 Using Hexane

If hexane is to be blended and named, the manufacturer must use in-house hexane standards which were gravimetrically blended using NBS weights in the place of NBS gas standards (which are unavailable) for the remainder of this Recommended Practice. The hexane must have been weighed-in to an accuracy of ±0.1% of the weight being added to a cylinder. The hexane in-house gravimetric standards must also be used in the monthly curve generation process (Sections 3.3.3 and 3.3.4) and the pre-analysis curve check (Section 3.4).

3.3.2 Definition of Linearity

The NBS Standard Reference Materials (SRM's) or gas manufacturers' Certified Reference Materials (gm-CRM's)*

listed in Table 2 and an instrument grade 99.9% pure nitrogen must be used to determine instrument linearity. A gas divider which can be used to dilute the highest concentration standard to at least three equally spaced lower concentrations is also acceptable for determining instrument linearity. For the purposes of these analytical procedures, a linear analytical instrument is defined as one which yields three intermediate points in the range of 1.0% CO to 8.0% CO, 250 ppm propane to 5000 ppm propane and/or 1.0% CO_2 to 7.0% or 14.0% CO_2 which deviate by ±2.0% of point** or less from

*CRM's refer to gas standards prepared and analyzed by a gas manufacturer according to EPA-600/6-81-010 ("A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards SRM's"). CRM's are recognized by EPA as equivalent to SRM's for establishing traceability.

**±2.0% of point is ±2.0% of reading. For example, if a reading of a certain gas is 6.0% CO, ±2.0% of 6.0% CO is ±0.12.% CO.

Table 2

SRM's or Gas Manufacturers' CRM's
Used to Determine Instrument Linearity*

Propane in N_2	Allowable Deviations For Linear Instruments
250 ppm	±5 ppm
500 ppm	±10 ppm
1000 ppm	±20 ppm
2500 ppm	±50 ppm
5000 ppm	±100 ppm
CO in N_2	
1.0%	±0.02% CO
2.0%	±0.04% CO
4.0%	±0.08% CO
8.0%	±0.16% CO
CO_2 in N_2	
1.0%	±0.02% CO_2
3.0%	±0.06% CO_2
4.0%	±0.08% CO_2
7.0%	±0.14% CO_2
14.0%**	±0.28% CO_2

*Instrument-grade 99.9% pure nitrogen must also be used to establish the instrument zero. The gas manufacturers' gravimetric hexane standards should be used to determine instrument linearity when hexane is to be analyzed.

**This CO_2 standard must be used in the linearity check if the CO_2 concentration to be named is over 7.0%. The 1.0% CO_2 standard can be dropped from the check in this situation.

a straight line drawn from the point determined by the zero gas to the highest calibration point. To be considered linear, the difference between the concentrations indicated by the intermediate points and the straight line must not exceed ±2.0% of the concentration values of the intermediate points. The range of allowable deviations from the straight line are also shown in Table 2.

Linearity need only be determined once per year on a particular instrument, unless service is performed on the instrument, in which case the linearity check must be conducted immediately after service is completed. Also, in the case of THC analyzers, if either the FID fuel or support air is changed, a linearity check must be conducted immediately thereafter.

3.3.3 Generation of Monthly Calibration Curve for Linear Instruments

If a linear instrument is to be used in the analysis of I/M calibration gases, at least once per month a calibration curve must be generated on the instrument in the range that is to be used to analyze the I/M calibration gas.

A minimum of six cylinders must be used to generate the calibration curve. One cylinder must be instrument grade 99.9% pure nitrogen, two other cylinders must be undiluted NBS-SRM's or gm-CRM's which are above and below the concentration of the I/M calibration gas to be named, and the other three cylinders can be gas manufacturer primary standards which have a minimum accuracy of ±2.0% to NBS - SRM's or gm-CRM's or other gas concentrations obtained by using a gas divider to dilute either an NBS SRM or gm-CRM or primary standard. Instrument responses for the five points other than the zero point should be approximately equally spaced on the range of the instrument which is to be used to name the I/M calibration gas. For example, if a 3.0% CO I/M calibration gas is to named, instrument responses could be obtained at 1.0% CO, 2.5% CO, 4.0% CO, 6.5% CO, and 8.0% CO. The 1.0% and 8.0% CO could be NBS-SRM's or gm-CRM's, with the others being either primary standards or gas concentrations obtained by diluting the NBS-SRM, gm-CRM's, or primary standards.

An equation must be calculated from the instrument response for the six gases. The labeled values of the cylinders analyzed must be the independent variable, with their responses being the dependent variable. If all points are within ±0.5% of the equation, the equation may be used to name I/M calibration gases in this Recommended Practice. Inability to satisfy this criterion with an equation is an

indication of improperly named primary standards, a malfunctioning gas divider, and/or malfunctioning analysis instrumentation. Rectifying these problems will likely result in the criterion being satisfied.

It is suggested that if an equation yields a calibration line which meets the above criteria, but calibration points do not appear to be randomly distributed above or below the line (e.g., there is a cluster of nearby points on one side of the line and another cluster or clusters on the other side) then a higher-order equation should be generated from the calibration points. This will increase the accuracy of the I/M calibration gas naming process. However, no inflection points are allowed in this higher-order equation in the range of data (see discussion of inflection points in the next section). The higher order curve must also meet the $\pm$0.5% of point criterion stated above.

3.3.4 Generation of Monthly Calibration Curve for Non-Linear Instruments

If a non-linear instrument is to be used to name I/M calibration gas, at least once per month a calibration curve must be generated on the instrument in the range that is to be used to analyze the I/M calibration gas.

A minimum of eight cylinders must be used to construct the calibration curve. One cylinder must be instrument-grade 99.9% pure nitrogen, two other cylinders must be undiluted NBS-SRM's or gm-CRM standards which are above and below the concentration of the I/M calibration gas to be named, and the other five cylinders can be primary standards or gases obtained by using a gas divider to dilute either an SRM, gm-CRM, or a primary standard. Instrument responses for the seven points other than the zero point should be approximately equally spaced on the range which is to be used to name the I/M calibration gas.

A polynomial equation must be calculated from the instrument responses to the eight gases obtained during this step. The labeled values of the cylinders must be the independent variable, with their responses being the dependent variable.

No inflection points* are allowed in the equation of the curve generated from analysis of the eight gases over the range of the data. If an inflection point occurs in an

*Inflection points can be determined by taking the second derivative of the resultant calibration curve equation, setting it equal to zero, and evaluating over the range of 0 to 100% full scale on the given range.

equation in the range of the data, a lesser order equation should be tried. If all points are within ±0.5% of the equation, the equation may be used to name I/M calibration gases. Inability to satisfy these criteria with a particular equation is an indicator of improperly named primary standards, a malfunctioning gas divider, and/or malfunctioning analysis instrumentation.

It is suggested that if a particular equation yields a calibration curve which meets the above criteria for non-linear instruments, but calibration points do not appear to be randomly distributed above or below the curve (e.g., there is a cluster of nearby points on one side of the curve and another cluster or clusters on the other side of the curve), then a higher-order equation should be generated from the calibration points. This will increase the accuracy of the I/M calibration gas naming process. However, no inflection points are allowed in this higher-order curve in the range of the data. The higher-order curve must meet the ±0.5% of point criterion stated in the previous paragraph.

3.4 Pre-Analysis Calibration Curve Check - All Instruments

Prior to the analysis of each batch* of I/M calibration gas cylinders,** the instruments being used to analyze the concentrations of the cylinders must be zeroed with instrument grade 99.9% pure nitrogen, spanned with an NBS-SRM or gm-CRM with a concentration at least 80% of full scale of the range being used to analyze the I/M gas (and adjusted if necessary), and then checked with two intermediate NBS or primary standards whose concentrations must be higher and lower than the I/M gas to be analyzed. These intermediate standards must be from the same group of standards that were used to develop the monthly curve. The equations generated by the monthly calibration curve for each instrument must be used in calculating concentrations for the intermediate standards from their responses. If the calculated concentrations do not match the labeled concentrations within ±0.5%, new calibration curves must be generated according to the procedures discussed in Sections 3.3.3 and 3.3.4.

*A batch is defined as more than five cylinders. The naming process for five or fewer cylinders is discussed in Section 3.6.

**As stated earlier, manufacturers may need to allow an incubation period between the time at which filling of the cylinder is complete and the time at which the analysis of the cylinder begins.

3.5 Analysis of I/M Calibration Gas Cylinders

3.5.1 Dependence on Previous Analysis of Bulk Mixture or Mixture Stream

Manufacturers have many different techniques for filling cylinders. In some of these techniques, an analysis is performed on each component in the mixture prior to filling a batch of cylinders. Examples of these techniques are where analyses are performed on a bulk homogeneous mixture, or performed continuously on a mixture of gas from the raw components that flow to the individual cylinders. Other techniques use no analysis other than that of the pure components. For example, a manufacturer may mix components together by partial pressures into a cylinder without analyzing the mixture.

The first step in the analysis process is the determination of homogeneity in the I/M gas batch. For filling techniques in which a previous analysis on every component except the diluent has been performed on the bulk homogenous mixture or on the mixture stream (as the cylinders are being filled), the gas manufacturer need only perform the homogeneity check on one component in every filled I/M cylinder. Where previous analysis of every component except the diluent of the bulk mixture or mixture stream has not been performed, the homogeneity check must be performed on every component in every I/M cylinder.

3.5.2 Homogeneity Check

No more than 1 hour may elapse between the time at which the calibration curve is checked and the time at which the homogeneity check of I/M cylinders begins. The homogeneity check is conducted by performing one analysis of the same component in every cylinder. Instrument drift must be determined and compensated for by reintroducing a primary standard with concentration between 80% and 100% of full scale after analysis of every five I/M cylinders. Adjustments must be made to the analyzer if the span drift exceeds $\pm$0.5%. If an adjustment is made to the analyzer to compensate for drift after the analyses of 5 I/M cylinders, those 5 cylinders must be reanalyzed after the adjustment is made. One other procedure which can be used in compensating for drift is discussed in Appendix 3.

A mean response is calculated from all of the analyses of that component in the I/M cylinders. Any cylinder with a response which exceeds $\pm$0.5% of the mean response can be reanalyzed. If reanalyzed and still found to exceed $\pm$0.5% of the mean, it must be rejected. If any one of the rejected

cylinders is reanalyzed and found to be within ±0.5% of the mean response, the cylinder can be reaccepted as a part of the batch.

3.5.3 Determination of Component Concentrations

A random sample of 10% of the batch and no less than six cylinders must be selected from the batch for the purpose of determining the concentrations of each of the components in the batch. In some cases, such as with high pressure cylinders, a gas manufacturer may blend gas mixtures directly into the cylinders by partial pressure. In such cases, the size of the batch is defined by the number of cylinders being blended at one time.

In other cases, such as with low pressure cylinders, a gas manufacturer must first blend a bulk homogeneous mixture into a large storage vessel and then transfer portions of the mixture into the individual cylinders that will utlimately go to the gas user. In this case, the size of the batch is defined by the amount of gas blended into the bulk storage vessel. For instance, assume that a gas manufacturer uses a bulk container to blend enough gas to fill 200 low pressure cylinders. Once the bulk mixture is blended and homogenized, the manufacturer then transfers the gas mixture from the bulk container to individual low pressure cylinders using a manifold which accommodates 20 cylinders at a time until all 200 cylinders have been filled. In this example, the batch size would be 200 cylinders. The 10% sample for analysis must be selected randomly from the entire batch.

If the mixtures are two-component mixtures (such as CO in N_2), any appropriate instrument may be used to analyze the components in the representative sample. However, if the mixtures are three-component mixtures of CO and propane (or hexane) in N_2, a gas chromatograph (GC) which is appropriately fitted to completely remove all other components from the analysis of the subject component must be used to analyze all components in the representative sample, whenever the gas concentrations are greater than 4% CO and/or 500 ppm propane (or 250 ppm hexane). In cases where the mixtures are three-component or four-component mixtures containing CO_2, a gas chromatographic analysis is also required.

Each component in each cylinder of the representative sample must then be analyzed. For mixtures of three or four components, each component must be analyzed simultaneously in each bottle (if the manufacturer has several GC's), or one component must be analyzed in every cylinder before the next component is analyzed.

Instrument drift must be determined and compensated for by reintroducing an NBS-SRM or gm-CRM or primary standard with concentration between 80% and 100% of full scale after the analysis of every 5 or fewer cylinders in the representative sample. Adjustments must be made to the GC if the span drift between any two analyses of the standard is ±0.5% or greater. If an adjustment is made to the GC to compensate for drift after the analyses of 5 I/M cylinders, those 5 I/M cylinders must be reanalyzed after the adjustment is made. One other procedure which can be used for compensating for drift is discussed in Appendix 3.

After analyses of all components is complete, a mean concentration is calculated for each component using the response for each component in the monthly equations as developed in Sections 3.3.3 and 3.3.4.

If all cylinders in the representative sample have component concentrations within ±0.5% for each component, the calculated mean concentration for each component in the representative sample can be used as the concentration for each component in the entire batch.

If any cylinder in the representative sample has a component with concentration that exceeds ±0.5% of the mean concentration for that component, all of the cylinders in the batch must be analyzed for that component. If the mixture being analyzed is a three or four component mixture, GC analysis must be performed on the entire batch for that component. For a two component mixture, any process instrument may be used. However, drift must be determined and compensated for during these analyses in the same manner as for the representative sample. An alternative procedure for compensating for drift is discussed in Appendix 3. A mean concentration is calculated for the entire batch from this analysis. Cylinders with concentrations exceeding ±0.5% of the mean concentration must be rejected. The mean concentration of the remaining cylinders is then calculated for that component. All cylinders remaining in the batch can then be labeled with the mean concentration for that component.

3.6 Analysis of Five or Fewer Cylinders

For a batch of five or fewer cylinders, each component in each cylinder must be analyzed twice. The response for each cylinder is then the average of the two measurements. The component concentrations should then be calculated in the same manner as for the representative sample described in Section 3.5.3.

3.7 Calculating the Accuracy of I/M Calibration Gas

A summary of the maximum allowed working tolerances for each step of the analysis process is shown in Table 3.

Table 3

Summary of Working Tolerances

Error Source	Allowed Tolerance
Monthly curve generation	±0.5%
Pre-analysis curve check	±0.5%
Homogeneity check - batch	±0.5%
Determination of component concentrations in representative sample	±0.5%

If the I/M gas has been blended and named according to this procedure and with the maximum allowable error tolerances listed in Table 3, the gas may be labeled with an accuracy of ±2.0% to NBS. The methods used in arriving at this accuracy are discussed in Appendix 4.

Some states may desire to order gases to better than a ±2.0% accuracy. In these cases, manufacturers will have to use more stringent working tolerances than those in Table 3. Manufacturers must use the methods outlined in Appendix 4 to calculate accuracies for gases ordered to be named according to this Recommended Practice but with better than ±2.0% to NBS accuracies.

3.8 Cylinder Labeling and Documentation

All I/M calibration gas cylinders ordered and named according to these procedures must be labeled with a tag which contains at a minimum the following information:

(i) Cylinder number, except in the use of low-pressure cylinders, where a batch number is required.

(ii) Concentration of hydrocarbons (in ppm - either hexane or propane), CO (in mol %), and CO_2 (in mol%) in cylinder gas (determined from Section 3.5.3), and accuracy specification (e.g., ±2.0%, or other as determined with methods in Appendix 4.

(iii) Balance gas (diluent).
(iv) Analysis date.
(v) Cylinder numbers of NBS and primary standards used in determining instrument calibration curves.
(vi) Vendor name.
(vii) Expiration date of cylinder (see below).
(viii) The statement that "This gas has been named in accordance with the EPA Recommended Practice for Naming I/M Calibration Gas."

The expiration date is the date beyond which the manufacturer does not suggest using the gas mixture to calibrate an analyzer. The length of time of use may vary with different mixtures.

The gas manufacturer must retain calibration curve data on each batch analysis of I/M calibration gas for a minimum period of 2 years. The data should include cylinder numbers of all standards used in the practice, and should allow someone to determine if the naming process has been performed correctly.

3.9 Audits of I/M Calibration Gases

A formal audit of I/M calibration gas which has been named according to this practice is not necessary prior to the sale and delivery of the I/M calibration gases. However, it should be remembered that State auditors will likely be checking the accuracies of calibration gases used with inspection analyzers. Inspection stations with improperly labeled calibration gases will likely be required by auditors to suspend the conducting of inspections until the problem with their calibration gas is resolved. The labeling requirements of the Recommended Practice should assist all concerned parties in determining why a cylinder or group of cylinders was improperly labeled.

The EPA may, from time to time, conduct audits of I/M calibration gas by acquiring on the open market cylinders named according to the Recommended Practice and analyzing these cylinders. The results of such audits are likely to be published by the EPA for the benefit of I/M programs.

3.10 Age of I/M Calibration Gas

Once a cylinder of I/M calibration gas has been properly named, it is assumed to have the same concentration until it is nearly empty,* regardless of how slowly it is used or how

*A cylinder is normally considered empty when the pressure in the cylinder drops to one-tenth of its original pressure.

much time expires between the time it is named and the time it is sold. EPA believes that this is a good assumption, since I/M calibration gases are high enough in concentration so that interior cylinder wall absorption does not materially affect the cylinder's concentration. This is a problem which is limited more to much lower concentration cylinders.

Appendices

Appendix 1

EXCERPT FROM: 45 FR 34808, MAY 22, 1980,

EMISSION PERFORMANCE WARRANTY REGULATIONS

§ 85.2217 Calibrations, adjustments.

(a) Equipment shall be calibrated in accordance with the manufacturers' instructions.

(b) Within one hour prior to a test, the analyzers shall be zeroed and spanned. Ambient air is acceptable as a zero gas; an electrical span check is acceptable. Zero and span checks shall be made on the lowest range capable of reading the short test standard.

(c) Within eight hours prior to a loaded test, the dynamometer shall be checked for proper power absorber settings.

(d)(1) The analyzers shall have been spanned and adjusted, if necessary, using gas traceable to NBS standards ± 2% within one week of the test. These span gases shall have concentrations either:

(i) Between the standards specified in this subpart and the jurisdictions inspection standards for 1981 model year light duty vehicles, or

(ii) Be within −50% to +100% of the standards in this subpart.

(2) For analyzers with a separate calibration or span port, CO readings using calibration gas through the probe and through the calibration port shall be made; discrepancies of over 3% shall require repair of leaks. No analyzer adjustments shall be permitted during this check.

Appendix 2

Step	Procedure
1	Check for impurities in pure components.
2	Determine whether instrument response is linear or non-linear.
3	Generate a monthly equation for each instrument to be used with NBS and other standards.
4	Fill I/M cylinders. Hold for incubation period, as necessary.
5	Check monthly equation with several gases used to generate monthly equation.
6	Perform homogeneity check on one component in all cylinders. Check to see that all cylinders are within $\pm$0.5 of mean response.
7	Randomly select a representative sample of 10% of the batch and no less than six cylinders.
8	Analyze each component in mixture. For two component mixtures any process instrument. For three and four component mixtures GC must be used, except for low concentration CO-propane (or hexane)-N_2 mixtures.
9	Calculate mean concentrations of components in representative sample. Check to see that all cylinders in representative sample are within $\pm$0.5% of mean concentrations for each component.
10	Calculate accuracy of process (or use $\pm$2.0%).
11	Label cylinders.

Appendix 3

Alternative Drift Procedure

This procedure can be used to compensate for drift in either the homogeneity check of the the batch or the concentration determination in the representative sample. In this procedure, a sample is selected at random to serve as a reference gas. The reference gas should be analyzed before the rest of the cylinders are analyzed and after the analysis of every subgroup of five or fewer cylinder in the batch. No analyzer adjustments are permitted during the analysis process.

The response of each I/M cylinder is then adjusted for drift with the following equation:

$$R_{i/mc} = R_{i/muc} \times \frac{Ris1}{Ris1 - \frac{N}{Q}(Ris1-Ris2)}$$

where

$R_{i/mc}$	=	the corrected response of the I/M cylinder
$R_{i/muc}$	=	the uncorrected response of the I/M cylinder
Ris1	=	the response of the reference gas before analysis of the subgroup of I/M cylinders
Ris2	=	the response of the reference gas after the analysis of the subgroup of the I/M cylinders
Q	=	number of segments between analyses of the reference gas.*
N	=	the Nth cylinder in the analysis of the subgroup.

This equation develops a ratio with which to correct the response of the I/M cylinder. The ratio is essentially a factor which measures the drift of the reference gas, corrects it to the time at which the I/M cylinder was analyzed, and applies it to the response of the I/M cylinder. Drift is assumed to be linear between analyses of the reference gas. For example, if an instrument drifted -0.5% between analyses of the reference gas and four I/M cylinders were analyzed between analyses of the reference gas, use of the ratio would say that the magnitude of drift at the time of analysis of the first cylinder was -0.1%. The ratio would then multiply the uncorrected response of the I/M

*For example, if 5 cylinders are analyzed between analyses of the reference gas, there are six potential segments of drift, one between analysis of each cylinder (RG-1-2-3-4-5-RG).

cylinder by 1.001 to obtain the corrected I/M cylinder response. This method of compensating for drift is identical to the method which is suggested in the naming of gm-CRM's.

The drift from one analysis of the reference gas to the next analysis of the reference gas must not exceed ±0.5%. If it does, the homogeneity check or concentration determination must be restarted. Once all I/M cylinders have been analyzed and corrected for a drift, a mean response is calculated. Cylinders whose responses differ from the mean response by more than ±0.5% of the mean response must be rejected as outliers. The remaining cylinders can then be labeled with the mean concentration.

Appendix 4

Accuracy Discussion

The model used to calculate the accuracies of I/M calibration gas is one that involves estimating the total uncertainty, U, with the following equation. This method is recognized by the National Bureau of Standards and has been widely used throughout the industry.*

$$U = (B + t_{90.0}S)$$

where

B is the bias limit

S is the precision error index

t is the 90th percentile point for the two-tailed Students "t" distribution. The t value is a function of the number of degrees of freedom used in calculating S. For small samples, t will be large and for larger samples t will be smaller, approaching 1.65 as a lower limit. The use of the t arbitrarily inflates the limit U to reduce the risk of underestimating S when a small sample is used to calculate S.

For the Recommended Practice, we are assuming that the sum of the bias errors is zero. One example of a bias error is the interference of CO on propane measurements with a THC analyzer. However, for three component mixtures (such as CO and propane in N_2) we have required that the representative sample be analyzed with GC techniques so that the bias errors would be close to zero. The value of S is calculated by the root mean square of the remaining precision errors, namely,

Monthly Calibration Curve	±0.5%
Pre-Analysis Curve Check	±0.5%
Homogeneity Check - Batch	±0.5%
Concentration Determination - Representative Sample	±0.5%

*The 95th percentile point has also been used as a t-factor.

The root mean square of these sources of errors at ±0.5% is ±1.0%.* The model now takes on the form $U=\pm t_{90}$ (1.0%). The t_{90} factor is taken from the two-tailed Students "t" distribution with 10% of the area under the distribution falling in the tails. These factors are shown in Table 4. The number of degrees of freedom is the sample size. For example, if a manufacturer makes a batch of 30 cylinders, the degrees of freedom is 30, and the t_{90} value is 1.697. The uncertainty then becomes (±1.0%)x(1.697)=±1.697%. The manufacturer should round this off to the nearest 0.1%, so this becomes ±1.7%.

In Section 3.7 "Calculating the Accuracy of I/M Calibration Gas" of the Recommended Practice, we stated that manufacturers following the practice and using the maximum allowable working tolerances for the four sources of error of ±0.5% could label the gas as having an accuracy of ±2.0%. Although the actual accuracy depends on the batch size (and the number of degrees of freedom), for batches of six cylinders or more the Student's t-factor is less than 2.0. This means that for any batch of six or more, the overall accuracy should be within ±2.0% (±1%x2). For batches of five or fewer, the recommended practice requires multiple analyses of each component in each cylinder (the number of analyses depending on the batch size) such that the Student's t-factor is less than 2.0.

Some States or I/M users may desire to order gas to better than ±2.0% accuracy. In these cases if the State or I/M user orders the gas blended according to the Recommended Practice, the manufacturer will have to reduce the working tolerances below ±0.5%. For instance, if the manufacturer is capable of reducing all of them to ±0.3%, a batch of 30 cylinders could be labeled with an accuracy of ±1.0%**. Manufacturers must use this technique to calculate the accuracy of a batch which is requested to be blended and named with the Recommended Practice with an accuracy different than ±2.0%.

*$(0.5^2 + 0.5^2 + 0.5^2 + 0.5^2)^{1/2}$

**$(0.3^2 + 0.3^2 + 0.3^2 + 0.3^2)^{1/2}$ (1.697) = ±1.0%

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Table 4

Student's t - Distribution for 10% of Area in Both t Calculations Combined*

Degrees of Freedom	Factor	Degrees of Freedom	Factor
1	6.314	21	1.721
2	2.920	22	1.717
3	2.353	23	1.714
4	2.132	24	1.711
5	2.015	25	1.708
6	1.943	26	1.706
7	1.895	27	1.703
8	1.860	28	1.701
9	1.833	29	1.699
10	1.812	30	1.697
11	1.796	40	1.684
12	1.782	60	1.671
13	1.771	120	1.658
14	1.761	Normal Distribution	1.645
15	1.753		
16	1.746		
17	1.740		
18	1.734		
19	1.729		
20	1.725		

*Hamburg, Morris, Statistical Analysis for Decision Making, 2nd edition, Harcourt Brace Jovanovich, Chicago, 1977, page 704.

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Technical Report

EPA RECOMMENDED PRACTICE FOR NAMING I/M CALIBRATION GAS: A DISCUSSION FOR I/M PROGRAMS

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Technical Support Staff
Emission Control Technology Division
Office of Mobile Sources
Office of Air and Radiation
U.S. Environmental Protection Agency
Ann Arbor, Michigan 48105

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Abstract

This report explains how calibration gases are used in I/M programs, and introduces a Recommended Practice for gas manufacturers to use when naming I/M calibration gas cylinders. Details of the Recommended Practice are presented in a separate report entitled "RECOMMENDED PRACTICE FOR NAMING I/M CALIBRATION GASES" (EPA-AA-TSS-83-8-B). States are encouraged to procure gases named according to this Recommended Practice for their own use, and to require licensed inspection stations to procure them to ensure that they are obtaining accurate calibration gases which meet the terms of the Emission Control System Performance Warranty, and to improve the general quality of their I/M programs.